MATERIALS SCIENCE

Response to Comment on "Improper molecular ferroelectrics with simultaneous ultrahigh pyroelectricity and figures of merit"

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Szafrański and Katrusiak stated that [Hdabco]ClO$_4$ and [Hdabco]BF$_4$ are proper ferroelectrics and exhibit much smaller pyroelectric coefficients than our results. We disagree with the arguments and provide a detailed answer highlighting misunderstandings in their interpretation.

Szafrański and Katrusiak stated that the space group of the paraelectric structure of [Hdabco]ClO$_4$ and [Hdabco]BF$_4$ is $P4/mmm$ (1–4). In 2018, they overturned their previous results and suggested that the space group is $P4/nmm$ (5) according to neutron-diffraction measurements. While the subtle nature of $P4/mmm$ and $P4/nmm$ structures could be appreciated from the marked drop of the intensity of the reflections with the sum of Bragg indices $h + k$ odd, Szafrański and Katrusiak misused the reflection (034) in their neutron diffraction measurements [figure 4 of (5)], which unfortunately did not obey the Bragg indices $h + k$ odd (6). In the main text of (7), $P4/nmm$ structure was misused in Fig. 1, and the corrected structure is shown in Fig. 1, with the same size of √2*√2*1 supercell size as $Pm2_1n$ structure for direct comparison. The misused plot does not affect the conclusions since all the calculations were based on the ferroelectric $Pm2_1n$ structures.

Szafrański and Katrusiak also stated that the one-component order parameter is inapplicable for improper ferroelectrics and the rotation (θ) and the polarization (P) are not related. However, the coupling terms of the equation include not only θP but also higher-order coupling terms (7). A single rotational mode (primary order parameter) was found to induce improper ferroelectricity in perovskite oxides (8). Similar coupling terms of the Landau type free energy model can be found in improper ferroelectrics including rare-earth molybdates, propionates, and boracites (9). More recently, improper ferroelectric di-n-butylaminium trifluoroacetate used the same form of the equation (10). Furthermore, in figure 2D of (11), the angle of [Hdabco]BF$_4$ changes at the first-order transition (155 K) with obvious decreases of the polarization. Therefore, θ(T) and P_s(T) are related. For improper ferroelectricity, one important feature is that the dielectric constant does not obey the Curie-Weiss law, but it does not mean that it should show a minor change of dielectric constant at Curie temperature (T_C) as claimed in (11). For example, a large change in dielectric constant from ~20 to >1200 at T_C has been observed in improper ferroelectric TMCM-MnCl$_3$ (12). As evidenced in figures 2A and S9B of (7), [Hdabco]ClO$_4$ and

[Hdabco]BF$_4$ films do not follow the Curie-Weiss law, also indicative of their improper feature.

The pyroelectric coefficient is described as the change in the electric charge per unit of surface area (i.e., the change of surface charge density) with a temperature change of 1°C. The pyroelectric coefficient (p) is equal to the negative derivative of spontaneous polarization (P_s) with respect to temperature (T), i.e., $p = -\frac{dP_s}{dT}$ (13). The total value of p is composed of four substantial parts (14): the primary pyroelectric effect caused by the change of spontaneous polarization with temperature fluctuations, the secondary pyroelectric effect arising from the piezoelectric effect induced by the thermal expansion and the mechanical strain, the tertiary pyroelectric effect that generates a polarization change caused by the spatial strain gradients that can be produced by deformation during nonuniform heating or cooling, and the field-induced pyroelectric effect determined by the temperature-dependent dielectric constant of materials with an external electric field. In our experiment, p of the samples was measured by a pyroelectric test system [see Methods of (7)] on the basis of the Byer-Roundy method, a recognized approach for pyroelectric coefficient measurements (15). In this measurement, the variation of spontaneous polarization generates a displacement current I described by $I = Ap(T)\frac{dT}{dt}$, where A is the surface area normal to the polar axis, and $p = -\frac{dP_s}{dT}$ is the pyroelectric coefficient at temperature T. Therefore, the pyroelectric coefficient can be given by $p(T) = \frac{I}{A\frac{dT}{dt}}$. When d$T$/d$t$ is held constantly over the operating temperature range, the measured current I could give a direct plot of $p(T)$ over that corresponding temperature range. In our experiment, the dT/dt of 2°C min^{-1} was held as a constant, and there is no external electric field applied on the samples. It is suggested that the measured p involves the primary pyroelectric
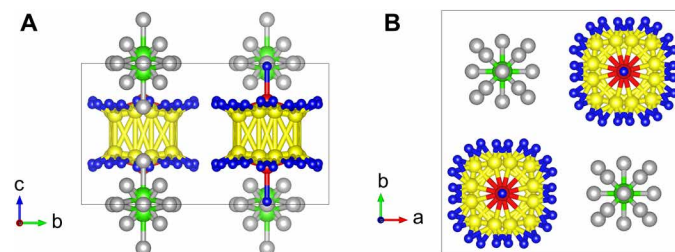

Fig. 1. Molecular structure of [Hdabco]ClO$_4$. The molecular structures of high-temperature $P4/mmm$ phase viewed along crystalline a-axis (**A**) and c-axis (**B**) direction, with √2*√2*1 supercell size for the same size as the $Pm2_1n$ structure.

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effect and the secondary pyroelectric effect, as our film samples deposited on the substrates would be affected by the clamping force between the films and the substrates. Differently, Szafrański and Katrusiak calculated p with the equation $p = \mathrm{d}P/\mathrm{d}T$, in which the P of the material is extracted from the P-E loops measured at different temperatures. The samples of Szafrański and Katrusiak are free-standing single crystals, and there is no mechanical strain caused by the substrate like our films. In addition, the P-E loop is stimulated by an electric field higher than the coercive field (10 kV cm^{-1}), which is also different from our measurement in which p was tested without the applied electric field. Moreover, as pointed out by Szafrański and Katrusiak, the calculated p derived from the equation $p = \mathrm{d}P/\mathrm{d}T$ is affected by the setting of the step of $\triangle T$. It is thus believed that the difference in the material forms and measurement methods leads to the different pyroelectric coefficients between our results and those of Szafrański and Katrusiak.

It is also logical that we compared the pyroelectric coefficient of [Hdabco]ClO$_4$ at its T_C with those of other materials at a temperature lower than their T_C. In contrast to the typical ferroelectrics that require poling for the macroscopic pyroelectric response, the pyroelectric signal in our [Hdabco]ClO$_4$ films can be obtained without poling because of the spontaneous formation of the orientated polarization during the growth of [Hdabco]ClO$_4$ [figure S5 of (7)]. Because of the self-poling effect, when operating cyclically across T_C, no obvious decay in p was observed in [Hdabco]ClO$_4$ films [figure S7 of (7)], suggesting that the high pyroelectric response occurring at T_C is reversible. In contrast, most conventional ferroelectrics lose their macro pyroelectric activity at temperatures above T_C, and thus, they have to operate under a temperature below T_C.

The argument on the discrepancy between our polarization results and those of (11) is attributed to the differences between films and single crystals. It is well known that the polarization of ferroelectrics is largely affected by the form of the materials (i.e., powders, single crystals, and films) and external stimuli. For example, the polarization of films is always different from that of freestanding bulks (16–19). Even in films, [Hdabco]ClO$_4$ shows a higher polarization when deposited on a Pt/TiSiO$_2$/Si substrate than that on Cu metal or Au-coated SiO$_2$ substrates (20). It is believed that the stress induced by substrates and the deposition process leads to the higher polarization of our films than that of single crystals of (11). The differences in polarization are also due to field strength applied on the samples. As shown in figure 2A of (11), while the polarization of ~4.5 μC cm^{-2} was obtained under an electric field of ~20 kV cm^{-1}, a higher polarization (e.g., 6 μC cm^{-2}) can be obtained with a larger electric field (7). Also, because of the low dielectric loss, a high field exceeding 100 kV cm^{-1} can be applied without breakdown. The different T_C values are attributed to the fact that the ferroelectric phase in polarization field (P-E) loop is induced by a high electric field, whereas the T_C from differential scanning calorimetry (DSC) and dielectric spectroscopy is measured without a high field. This has been extensively reported in various ferroelectrics (21–24). Therefore, even under a temperature 5 K higher than T_C, the high field could induce a ferroelectric P-E loop in [Hdabco]ClO$_4$. Besides, by comparing the polarization as a function of temperature of our [Hdabco]BF$_4$ films with figure 2D of (11), it is clear that our result shows a steeper polarization-temperature curve at T_C without smearing, which is different from that pointed out by Szafrański and Katrusiak (11).

[Hdabco]ClO$_4$ and [Hdabco]BF$_4$ belong to the organic-inorganic hybrid ferroelectrics consisting of organic molecular groups and inorganic ions, e.g., (TMFM)$_x$(TMCM)$_{1-x}$CdCl$_3$, (EA)$_2$(MA)$_2$Pb$_3$Br$_{10}$, [(CH$_3$)$_4$N][FeCl$_4$], and [Ph$_2$(^{i}PrNH)$_2$P]X [X = Cl, Br, I], which have been commonly referred to as molecular ferroelectrics in literatures (25–28). Therefore, it is proper to label these structures as molecular ferroelectrics (20, 29).

Szafrański and Katrusiak claimed that our work concealed their original report on the ferroelectricity in dabco monosalts and overlooked their structural determinations in the Cambridge Structural Database. We reject this comment. The main content of our article is not the rediscovery of ferroelectricity of [Hdabco]ClO$_4$ and [Hdabco]BF$_4$, but the discovery of their high pyroelectric performance. Szafrański and Katrusiak apparently missed the main point of (7). In addition, we have properly cited the literature on ferroelectricity of dabco monosalts, including their works [references 21, 28, 29, 61, and 62 in (7)]. To confirm the first-order phase transition and crystal structure of our prepared [Hdabco]ClO$_4$, we conducted DSC and x-ray diffraction measurements and compared the literature results [Fig. 1 and figure S3 and table S1 of (7)] including those of Szafrański and Katrusiak (1, 4). They also commented that we incorrectly cited references 27 to 29 and should not cite references 30 and 31. The sentence cited with references 27 to 29 of (7) points out that improper ferroelectricity is induced by the coupling scheme of different distortions. References 28 and 29 describe the coupling scheme and the distortion phenomenon in the materials. The coupling scheme and the distortion phenomenon could induce improper ferroelectricity, as reported in reference 27. Therefore, we cited these three papers in (7). Besides, references 30 and 31 of (7) are classical references for the fundamentals of the Landau-Devonshire theory–based numerical calculations, which are the base for the Landau-Devonshire theory used for improper ferroelectricity. The citation of such classic work is proper and necessary.

REFERENCES AND NOTES

1. A. Katrusiak, M. Ratajczak-Sitarz, E. Grech, Stereochemistry and transformations of NH: N hydrogen bonds Part II. Proton stability in the monosalts of 1,4-diazabicyclo[2.2.2]octane. *J. Mol. Struct.* **474**, 135–141 (1999).

2. A. Budzianowski, A. Katrusiak, M. Szafrański, Anomalous protonic-glass evolution from ordered phase in NH···N hydrogen-bonded DabcoHBF$_4$ ferroelectric. *J. Phys. Chem. B* **112**, 16619–16625 (2008).

3. A. Olejniczak, M. Anioła, M. Szafrański, A. Budzianowski, A. Katrusiak, New polar phases of 1,4-diazabicyclo[2.2.2]octane perchlorate, an NH$^+$···N hydrogen-bonded ferroelectric. *Cryst. Growth Des.* **13**, 2872–2879 (2013).

4. A. Katrusiak, Proton dynamics in NH$^+$···N hydrogen bond in the paraelectric structure of 1,4-diazabicyclo[2.2.2]octane perchlorate. *J. Mol. Struct.* **552**, 159–164 (2000).

5. A. Olejniczak, M. Szafrański, A. Katrusiak, Pressure–temperature phase diagrams and transition mechanisms of hybrid organic–inorganic NH···N bonded ferroelectrics. *Cryst. Growth Des.* **18**, 6488–6496 (2018).

6. T. Hahn, *International Tables for Crystallography, Volume A: Space-Group Symmetry* (Springer, ed. 5, 2005).

7. W. Li, G. Tang, G. Zhang, H. M. Jafri, J. Zhou, D. Liu, Y. Liu, J. Wang, K. Jin, Y. Hu, H. Gu, Z. Wang, J. Hong, H. Huang, L.-Q. Chen, S. Jiang, Q. Wang, Improper molecular ferroelectrics with simultaneous ultrahigh pyroelectricity and figures of merit. *Sci. Adv.* **7**, eabe3068 (2021).

8. J. Young, J. M. Rondinelli, Improper ferroelectricity and piezoelectric responses in rhombohedral (A,A')B_2O$_6$ perovskite oxides. *Phys. Rev. B* **89**, 174110 (2014).

9. A. Shaulov, W. A. Smith, G. M. Loiacono, M. I. Bell, Y. H. Tsuo, Improper ferroelectrics for pyroelectric detection of infrared radiation. *Ferroelectrics* **27**, 117–121 (1980).

10. Z. Sun, Y. Tang, S. Zhang, C. Ji, T. Chen, J. Luo, Ultrahigh pyroelectric figures of merit associated with distinct bistable dielectric phase transition in a new molecular compound: Di-n-butylaminium trifluoroacetate. *Adv. Mater.* **27**, 4795–4801 (2015).

11. M. Szafrański, A. Katrusiak, Comment on "Improper molecular ferroelectrics with simultaneous ultrahigh pyroelectricity and figures of merit." arXiv:2107.00242 [cond-mat. mtrl-sci] (1 July 2021).

12. Y.-M. You, W.-Q. Liao, D. Zhao, H.-Y. Ye, Y. Zhang, Q. Zhou, X. Niu, J. Wang, P.-F. Li, D.-W. Fu, Z. Wang, S. Gao, K. Yang, J.-M. Liu, J. Li, Y. Yan, R.-G. Xiong, An organic-inorganic perovskite ferroelectric with large piezoelectric response. *Science* **357**, 306–309 (2017).

13. A. Agulyansky, Ferroelectric properties of niobium and tantalum fluoride compounds, in *Chemistry of tantalum and Niobium Fluoride Compounds* (Elsevier Science, 2004), chap. 7, pp. 217–251.

14. S. Jachalke, E. Mehner, H. Stöcker, J. Hanzig, M. Sonntag, T. Weigel, T. Leisegang, D. C. Meyer, How to measure the pyroelectric coefficient? *Appl. Phys. Rev.* **4**, 021303 (2017).

15. R. L. Byer, C. B. Roundy, Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *Ferroelectrics* **3**, 333–338 (1972).

16. K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, C. B. Eom, Enhancement of ferroelectricity in strained $BaTiO_3$ thin films. *Science* **306**, 1005–1009 (2004).

17. S. K. Singh, H. Ishiwara, K. Maruyama, Enhanced polarization and reduced leakage current in $BiFeO_3$ thin films fabricated by chemical solution deposition. *J. Appl. Phys.* **100**, 064102 (2006).

18. H. Liu, X. Gong, J.-E. Liang, X. Li, D. Xiao, J. Zhu, Z. Pu, Enhanced dielectric and ferroelectric properties of $Pb(Zr_{0.8}Ti_{0.2})O_3/Pb(Zr_{0.2}Ti_{0.8})O_3$ multilayer films. *Appl. Phys. Lett.* **91**, 122906 (2007).

19. Q. Pan, Z.-B. Liu, H.-Y. Zhang, W.-Y. Zhang, Y.-Y. Tang, Y.-M. You, P.-F. Li, W.-Q. Liao, P.-P. Shi, R.-W. Ma, R.-Y. Wei, R.-G. Xiong, A molecular polycrystalline ferroelectric with record-high phase transition temperature. *Adv. Mater.* **29**, 1700831 (2017).

20. Y.-Y. Tang, W.-Y. Zhang, P.-F. Li, H.-Y. Ye, Y.-M. You, R.-G. Xiong, Ultrafast polarization switching in a biaxial molecular ferroelectric thin film: [Hdabco]ClO_4. *J. Am. Chem. Soc.* **138**, 15784–15789 (2016).

21. J. H. Qiu, Q. Jiang, Effect of electric field on electrocaloric effect in $Pb(Zr_{1-x}Ti_x)O_3$ solid solution. *Phys. Lett. A* **372**, 7191–7195 (2008).

22. J. Han, W. Cao, Electric field effects on the phase transitions in [001]-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ single crystals with compositions near the morphotropic phase boundary. *Phys. Rev. B* **68**, 134102 (2003).

23. A. Tkach, P. M. Vilarinho, A. L. Kholkin, Structure–microstructure–dielectric tunability relationship in Mn-doped strontium titanate ceramics. *Acta Mater.* **53**, 5061–5069 (2005).

24. M. Poulsen, A. V. Sorokin, S. Adenwalla, S. Ducharme, V. M. Fridkin, Effects of an external electric field on the ferroelectric-paraelectric phase transition in polyvinylidene fluoride-trifluoroethylene copolymer Langmuir–Blodgett films. *J. Appl. Phys.* **103**, 034116 (2008).

25. W.-Q. Liao, D. Zhao, Y.-Y. Tang, Y. Zhang, P.-F. Li, P.-P. Shi, X.-G. Chen, Y.-M. You, R.-G. Xiong, A molecular perovskite solid solution with piezoelectricity stronger than lead zirconate titanate. *Science* **363**, 1206–1210 (2019).

26. X. Liu, S. Wang, P. Long, L. Li, Y. Peng, Z. Xu, S. Han, Z. Sun, M. Hong, J. Luo, Polarization-driven self-powered photodetection in a single-phase biaxial hybrid perovskite ferroelectric. *Angew. Chem. Int. Ed.* **58**, 14504–14508 (2019).

27. J. Harada, N. Yoneyama, S. Yokokura, Y. Takahashi, A. Miura, N. Kitamura, T. Inabe, Ferroelectricity and piezoelectricity in free-standing polycrystalline films of plastic crystals. *J. Am. Chem. Soc.* **140**, 346–354 (2018).

28. T. Vijayakanth, R. Pandey, P. Kulkarni, B. Praveenkumar, D. Kabra, R. Boomishankar, Hydrogen-bonded organo-amino phosphonium halides: Dielectric, piezoelectric and possible ferroelectric properties. *Dalton Trans.* **48**, 7331–7336 (2019).

29. P.-P. Shi, Y.-Y. Tang, P.-F. Li, H.-Y. Ye, R.-G. Xiong, De novo discovery of [Hdabco]BF_4 molecular ferroelectric thin film for nonvolatile low-voltage memories. *J. Am. Chem. Soc.* **139**, 1319–1324 (2017).